ACHIEVING OPACITY IN CERAMIC TILES: MICROSTRUCTURAL AND SPECTROPHOTOMETRIC ANALYSIS

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ABSTRACT

A major factor in obtaining stable colours in ceramic tiles is the use of agents that can cause opacity in transparent enamels. These agents are used as additives in enamel preparation, and the control of their effect during firing is fundamental, due the possible elimination or reduction of tonality variation during processing. The most widely used agents to cause opacity are zirconia (zirconium silicate: $ZrSiO_4$) and rutile (titanium oxide: TiO_2). Particle size, refraction index and volumetric fraction of the opacifying agent being used affect the enamel degree of opacity. This work therefore aims to evaluate the influence of the zirconia mass fraction on the opacity of a transparent enamel, based on microstructural aspects, mainly particle dispersion in the glaze matrix. A transparent frit for single firing was used; the frit was milled in a laboratory jar mill (#325 mesh) and fine zirconia was added (1% to 24%; mass fraction). The glazes obtained were homogenized (5min; jar mill) and compacted (25MPa) in cylindrical samples with wax (10% weight). The pressed samples were sintered (1100°C; 5min) after a dewaxing process. After sample preparation, microstructural (SEM and OM) and spectrophotometric analysis was carried out. The results showed the optimum addition fraction that causes complete enamel opacity.

Key words: *opacity; zirconium silicate; glazes; microstructure analysis; spectrophotometry.*

1. SUMMARY

Colour control plays a major role in ceramic enamel production. Tonality difference between products intended to have the same aspect currently constitute the biggest source of customer claims in the coverings market. On the other hand, the lack of tonality uniformity also harms production, resulting in a bigger percentage of rejection, productivity reduction and stock increase due the presence of several tonality classes for each product reference (Bernardin, 2002).

Tonality control has become more difficult due the complex design of new products that need several layers of decoration. The continuous effort applied in enamel compositions with cheaper raw materials has also caused some problems: different kinds of raw materials influence colour development. Also, the fast evolution of firing technology gives rise to colour variation in glazes, since in many plants the same product is fired in different types of kilns and firing cycles, due to product changes in the production line. There is a great interest in the ceramic industry in the development of robust enamel formulations, which allow attainment of constant colours in a wide range of processing conditions.

Frits based on multiple oxide silicate glasses are the main raw materials of enamel compositions used in the manufacture of ceramic products obtained by fast single firing processes (Tozzi, 1986; Enrique, 1996). Furthermore, oxide pigments are the most accessible colorants for the ceramic tile industry. Frits for opaque enamels contain zirconia (ZrO_2), which reacts at high temperatures with SiO_2, resulting in the precipitation of zirconium particles (Barson, 1997; Meinssen, 1997).

In this context, a major factor in achieving stable colours is the use of agents that act in opacifying ceramic enamels (Hevia, 2002; Tozzi, 1986; Enrique, 1996; Gutzow, 1995). These agents are used as additives in enamel processing, and their control during firing is fundamental; thus, this control allows the reduction of tonality variation (Gutzow, 1995; López, 2001).

The optical characteristics of glazes, glasses and enamels perceived by an observer are the result of light reflection and scattering, caused by small particles or discontinuous nuclei in their interior (Gutzow, 1995). The most important optical characteristics are those related to the amount (percentage) of specular reflection (which determines brightness) and the amount of transmitted light (which determines colour, depth, saturation, etc.), as a function of the fraction of diffusely transmitted light.

The opacity and covering characteristics of glasses and glazes depend on the amount of diffuse light reflected by the top surface, before reaching the bottom surface. For translucent glasses, most of the light must be transmitted and only part diffusely reflected.

The opacifying power, therefore, depends on light scattering by particles or nuclei present in the binary system, directly related to size, form, concentration and refractive index of the secondary phase (Kingery, 1976). Thus, maximum light scattering occurs, or in other terms, to maximize the diffuse reflection, secondary phase particles must have a sufficiently different refractive index related to the matrix, and must have a particle size similar to the wavelength of the incident light. Second phase concentration must be relatively high, in order to present a high number of diffuse reflectance points.

The refractive index of most glazes and ceramic enamels pertaining to silicate and borosilicate systems lies between 1.48 and 1.65. Therefore, the opacifying agents must have a substantially superior refractive index. Actually, the higher the refractive index of the opacifying agent, the whiter will be the glaze. The ideal opacifying agent must form very small particles in liquids of silica matrix, as well as being completely inert to the glass phase. Chemically, these agents must have high inertia and insolubility in the glass matrix at low temperatures, must precipitate at glass cooling range, and must have high solubility in glass at melting temperatures. As a result, the opacifying agents form by recrystallization of the liquid medium, forming very small crystals, resulting in high coverage. This mechanism forms most of the possible opaque glasses and glazes, including white zirconium frits and titanium dioxide enamels, used for glazing.

Another important characteristic of the opacifying agents is the fact that these materials must not present absorption coefficients situated in the visible spectrum, or in other terms, they must be transparent to wavelengths corresponding to visible light.

The choice of a specific opacifying agent depends both on the system to be opacified and the manufacturing process to be used, besides the type of substrate. For glazing, the type of enamel must have a higher coating effect due the use of relatively fine layers. In this case, it is preferable to use enamels made opaque by titanium dioxide.

In ceramic glazes the vitreous layers are relatively thicker, allowing the use of glazes or frits with a less efficient coating effect. Thus, it is recommended to use glazes and frits based on a zirconium silicate system, which presents a less yellow colour and is less soluble in the glass system. Tin dioxide (SnO_2) is also an excellent opacifying agent for use in ceramic glazes.

The degree of opacity of a glaze can be quantified by means of its respective opacifying agent absorption factor, measured by the Kubelka-Munk theory (K/S), calculated from the spectral reflectance curves (Eppler, 1990; Eppler, 1996), according to the relation:

$$\frac{K}{S} = \frac{(1 - R_{min})^2}{2R_{min}}$$

where K is the absorption constant, S the scatter constant and R_{min} the spectral reflectance in the wavelength in which the additive produces the minimum reflectance or the maximum light absorption, in this case, zirconia. Therefore, the larger the K/S value, the greater the opacifying effect caused by the ceramic additive on the enamel (Blonski, 1994; Booth, 1959).

It is a double flow theory, in which it is assumed that the radiation is composed of two radiation flows in opposing directions through a continuous medium. The theory has been widely used to relate the total diffuse reflection of a material with its scattering and its absorption.

The mathematical model of Kubelka-Munk can be used to describe the reflectance of opaque samples. The model considers the absorption and scattering that occurs in coloured samples of fixed thickness, and it is applied wavelength by wavelength through the visible region of the electromagnetic spectrum.

The reflectance of the sample in each wavelength depends on four factors: an absorption spectrum ($K(\lambda)$), a scattering spectrum ($S(\lambda)$), the sample thickness (x) and the reflectance spectrum of the substratum or base ($R_p(\lambda)$). The model considers the incident light to be collimated and the light that penetrates the sample is considered as scattered. While the light can spread in any direction, the model considers two liquid flows, directly above and directly below.

Zirconium oxide (ZrO_2) is a good opacifying agent, with an ample temperature range, particularly with enamels that have a low silica content. However, it increases glaze viscosity (Gutzow, 1995; Hevia, 2002). Zirconium silicate, with a refractive index of 1,92 and with a ZrO_2 mass content between 63% and 66%, is the most widely used opacifying agent for enamels fired between 940°C and 1300°C, having a lower cost compared with pure SnO_2 or pure ZrO_2.

The ZrO_2 introduced by the zirconium silicate addition reduces the glaze expansion coefficient, causing a better interface with the substrate. It also increases glass viscosity and stabilizes colours. In a different way to SnO_2, where glass body opacity occurs due to the insolubility of its small particles, the opacifying effect of ZrO_2 occurs because two immiscible glass phases form during fusion, or because crystal precipitation of ZrO_2 occurs. The opacity that ZrO_2 provides can be improved by the presence of Al_2O_3, ZnO, CaO, MgO and BaO. A high fraction of ZrO_2 in the composition implies a higher glaze firing temperature.

2. MATERIALS AND METHODS

In this study, a transparent single firing ceramic glaze was used. Its composition (in weight) was 92% frit (based on the ZnO and CaO system, or market equivalent), 8% kaolin and 50% water. The glaze was milled in eccentric mills to obtain a particle size distribution below 40μm (325 mesh). An eccentric mill (1000ml capacity) was used for all formulas, with alumina spheres as grinding media (330g). The milling time was 90min.

Zirconia powder was used as an opacifying agent (zirconium silicate, $ZrO_2.SiO_2$), 500 mesh, the particle size distribution most widely used in Brazil; which is the so-called zirconia flour. The mass fractions of zirconia added to each glaze composition were 1%, 3%, 6%, 12% and 24% (wt%).

The compositions were homogenized (5min, eccentric mill) and the paste pressed in a cylinder shape (25MPa) with 10% of wax addition (wt%). Then the samples were sintered at 1000°C for 5min, after an intermediate 700°C cycle of wax elimination (dewaxing step).

The sintered samples were analyzed using a spectrophotometer in the visible light region (400nm to 700nm) and microstructural analysis was also carried out. The Kubelka-Munk parameters and the spectral reflectance curves were obtained, measuring all glaze surfaces using a d8 (spherical) geometry, D65 light source and 10° observer angle, with specular component included. All five compositions were analyzed using the same conditions.

The degree of opacity of the each glaze composition was analyzed by means of the absorption and scattering coefficient relation (K/S), using spectral reflectance data.

3. RESULTS AND DISCUSSION

After mixture preparation, dilatometric analysis was performed to determine the softening temperature of each composition. A higher softening temperatures means that the glaze is more refractory. For sample 1, glaze with 1 wt% zirconia, the softening temperature was approximately 660°C; for sample 5 (24 wt% $ZrO_2.SiO_2$), this was 678°C (figure 1).

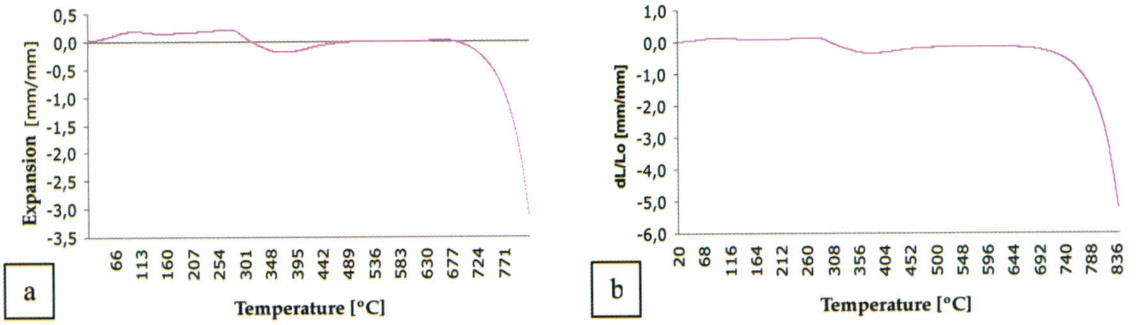

Figure 1. Expansion curves for (a) sample 1 (1 wt% zirconia) and (b) sample 5 (24 wt% zirconia).

The results confirm the effect of the rise of glaze softening temperature with the increase of zirconia mass fraction. Probably, melt viscosity is also increased. After sample thermal treatments, the spectral curves were measured to determine the reflectances as a function of the zirconia addition. From the K/S ratio, the reflectance curves were determined for all samples (figure 2).

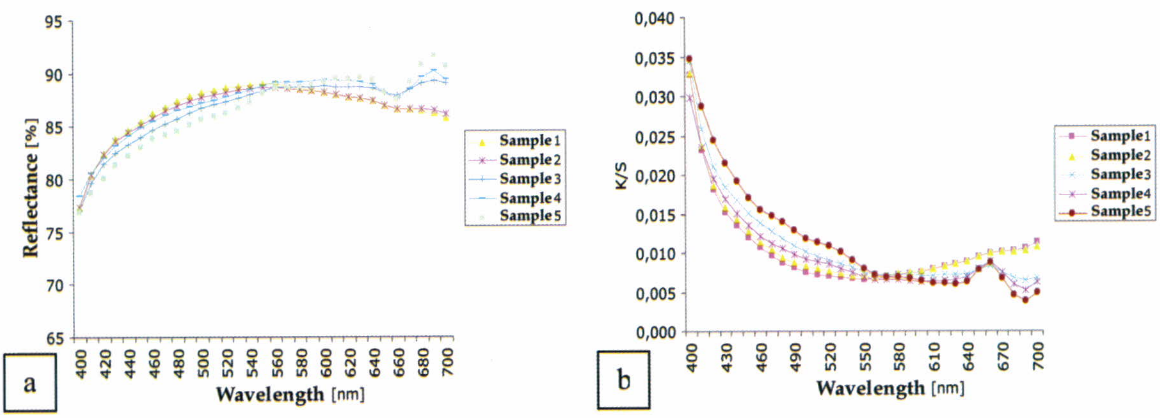

Figure 2. Reflectance (a) and K/S absorption factor (b) curves.

The results demonstrate that the sample with 24 wt% zirconia also presents the largest reflectance and the largest absorption for wavelengths between 400nm and 560nm, proving that the zirconia addition causes opacity of transparent glazes. Obviously, the degree of opacity rises with an increasing zirconia addition. Microscopic analysis shows that the zirconia particles are well dispersed in the glass matrix (figure 3). The zirconia particles are polyhedral, with a small particle size distribution. However, this can only be proven by a specific test on particle size distribution, which was not carried out.

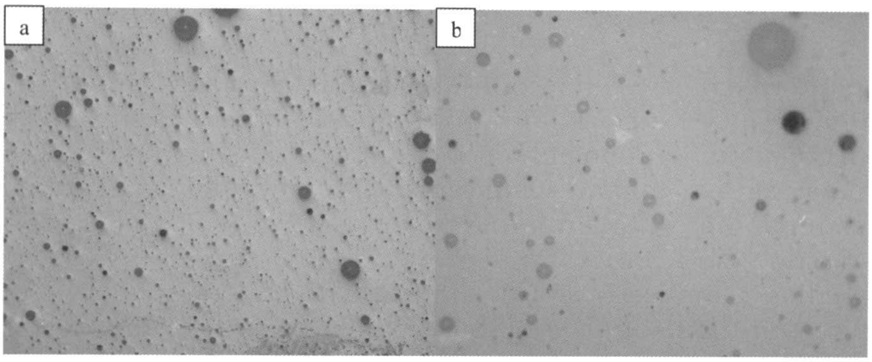

Figure 3. Sample micrographs (12 wt% de zirconia) (a) 50x magnification; (b) (100x) magnification.

4. CONCLUSION

The study clearly shows the opacifying effect of additives with a higher refractive index used in transparent frits (aluminosilicate glasses), as a basis for ceramic glazes. The zirconia powder used in this study was confirmed to be very efficient in opacifying the researched system. Microscopic analysis has clearly shown the efficiency of additive particle size reduction (zirconia, in this case) in glaze opacity. Particle size was apparently close to the wavelength of the incident light. However, this can only be proven by means of particle size analysis by LASER diffraction, which was not conducted in this preliminary study. Particles with sizes close to the wavelength of incident light are really effective in light scattering and consequently in the opacity of the system. The most efficient volumetric fraction of the additive phase was, obviously, the largest one (24 wt%). This fraction can be optimized by subsequent studies. The additive is well dispersed in the glass matrix, demonstrating that the mixture process was appropriately performed.

REFERENCES

[1] Bernardin, A.M. et al. Use of zirconia to achieve opacity in transparent enamels: characterization using Kubelka-Munk techniques. Castellón: Qualicer 2002, 2002.

[2] Tozzi, R. Glazes for fast-firing. Rimini: Assiceram Italian Ceramic Society, 1986.

[3] Enrique, J. et al. Evolution of ceramic tile glazes. Westerville: American Ceramic Society, Science of Whitewares, p.357-370, 1996.

[4] Barson, T. Frit: the engineered material. Ceram. Eng. Sci. Proc., n.18, v.2, p.28-36, 1997.

[5] Meinssen, K. Ceramic glaze materials: the top ten list. Ceram. Eng. Sci. Proc., n.18, v.2, p.308-319, 1997.

[6] Hevia, R. et al. Introducción a los esmaltes cerámicos. Castellón: Faenza Editrice Ibérica, Cyted Red VIII, 2002.

[7] Gutzow, I.; Schmelzer, J. The vitreous state. Heidelberg: Springer-Verlag Berlin, 1995.

[8] López, P.E. et al. Esmaltes y pigmentos cerámicos. Castellón: Faenza Editrice Ibérica, v.1, 2001.

[9] Kingery, W. D. et al. Introduction to ceramics. New York: John Wiley & Sons, 2nd ed., 1976.

[10] Eppler, R. A. Predicting the color of a ceramic glaze. New York: Ceramic Bulletin, v.69, n.2, p.228-230, 1990.

11] Eppler, D.; Eppler, R. Analyzing the color of reddish glazes. Ceram. Eng. Sci. Proc., n.17, v.1, p.77-87, 1996.

[12] Blonski, R. P. The effect of zirconia dissolution on the color stability of glazes. Ceram. Eng. Sci. Proc., n.15, v.1, p.249-265, 1994.

[13] Blonski, R. The effect of zircon dissolution and reprecipitation on the color development of glazes. Ceram. Eng. Sci. Proc., n.14, v.1-2, p.176-189, 1993.

[14] Booth, F.T. The principles of glaze opacity with zirconium silicate. Trans. Bri. Ceram. Soc., n.58, p.532-564, 1959.